



# **HISTORICAL ARSENIC OPERATIONS**

## **GLOBE PLANT DENVER, COLORADO**

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**EnviroGroup Limited**

***The environmental solutions company***

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## INTRODUCTION

This document provides a summary of arsenic and other metals processing and refining operations, with potential arsenic air emissions, that have been conducted at the Globe Plant at various times since its inception in 1886. The Globe Plant was initially constructed as a lead smelter, known at that time as the Holden Smelter. The history of the subsequent operations and their potential for producing arsenic air emissions can best be described by looking at four separate metals operations, as follows:

### Lead Smelting:

Lead smelting was the principal operation at the Globe Plant from the time the facility was constructed in 1886 until the smelting operation was discontinued in 1919.

Arsenic, present in low concentrations in the lead ore, would also have been present to some degree in the emissions from the blast furnaces and roasters.

### Arsenic Trioxide Refining:

Arsenic trioxide was recovered from lead smelter baghouse dust from 1910 until the operation was discontinued in 1926. From 1920 until 1926 the Globe Plant recovered and refined arsenic trioxide from the baghouse dusts of other lead smelters.

### Cadmium Roasting and Calcining:

Cadmium was recovered from lead smelter baghouse dust on a small scale as early as 1912 and cadmium recovery became the principal operation at the Globe Plant after arsenic trioxide operations discontinued in 1926. Two steps in the cadmium recovery process had potential for significant arsenic air emissions: roasting of lead smelter baghouse dust to concentrate the cadmium, and calcining of the concentrated dust. Later steps in the cadmium refining process; e.g., purification,

electroplating, and retorting, had less potential for arsenic emissions because most of the arsenic was eliminated by the roasting and calcining operations. Roasting operations ended in 1977 and calcining ceased in 1982, replaced by pyrometallurgical processes. The cadmium circuit was discontinued in 1993.

#### High Purity Metals Refining:

Only high purity metal, litharge, and bismuth recovery and refining operations have been conducted at the Globe Plant over the past five years. Arsenic emissions associated with these operations, as confirmed by air monitoring data, have been negligible.

The general nature and layout of the facilities during various time periods are shown on Figures 1 through 7. Key historic engineering drawings associated with the arsenic trioxide refining operations are included in Attachment A to this document. The maps on Figures 1 through 7 are based on various historic maps provided in a companion document summarizing historic lead operations (EnviroGroup 1998). The following sections discuss each of the above Globe Plant operations and their potential for arsenic emissions in more detail.

### **LEAD SMELTING OPERATIONS C. 1886 TO 1919**

The Globe Plant (known at the time as the Holden Smelter) was initially constructed as a lead smelter. Details of the historic lead smelting operations are provided in the companion document (EnviroGroup, 1998). Roasting and smelting of lead ore would have resulted in some arsenic air emissions due to the presence of arsenic in the ore. According to Iles (1902), arsenic concentrations in the lead smelter baghouse dust ranged from 1.5 to 5 percent; therefore, arsenic emissions can be estimated as a fraction of overall emissions, or as a fraction of lead emissions.

Controls of emissions from the smelting of lead were greatly increased with the addition of a 1200 foot long flue and bag house in 1891 (Iles, 1902) resulting in a 63% reduction in lead concentration in blast furnace smoke. The bag house was further expanded after 1905 under ownership of American Smelting and Refining Company.

## **ARSENIC TRIOXIDE PRODUCTION C. 1912-1926**

### Description of Process

Lead blast-furnace flue dust contains a certain amount of arsenic, depending on the arsenic content of the ore and the temperature of the furnace (i.e., the amount of arsenic oxide volatilized). According to Iles (1902), the arsenic content of the blast furnace baghouse dust at the Globe Plant in the 1890's was typically greater than 1.5 percent and rarely greater than 5 percent. This was consistent with ores predominantly from the Leadville area, which contained an average 0.1 percent arsenic (Guyard 1884). However, over time the Globe Plant began to process ore from more diverse sources, including Montana, Utah, and Mexico (Fell 1979); ores from some of these locations contained higher concentrations of arsenic (e.g. Parsons 1925). Recycling of baghouse dust from these ores back through the blast furnaces could result in dusts with arsenic concentrations in the 30 to 60 percent range (Carapella 1964, Parsons 1925).

The recovery and refining of arsenic trioxide from baghouse dusts with elevated arsenic concentrations was a two step process. First, arsenic trioxide was vaporized or sublimated from the dust by roasting at relatively low temperatures; other metals with higher volatilization temperatures, such as cadmium and lead, tended to remain in the dust. The roaster fumes were then routed through a series of brick flues known as "black arsenic flues", where the gas cooled and the arsenic trioxide condensed as crystals (e.g., see Carapella 1964, Hayward 1940, Parsons 1925 for descriptions of the arsenic refining process). Although most of the arsenic trioxide would have condensed and settled out in the flues, gases leaving the flues were conveyed to a dedicated portion of the baghouse for further capture of the product. In a similar process described by Parsons (1925), the

resulting black flue dust contained 90 to 92 percent arsenic trioxide, while in more modern refineries, arsenic trioxide levels in the black dust would be as high as 95 percent (Carapella 1964).

The second step of the arsenic trioxide refining process was conducted in the arsenic refinery (e.g., see Figure 3), where the black flue dust was roasted again to re-sublimate the arsenic trioxide. The fumes from the arsenic refining furnaces were routed through a second set of flues, called the "white arsenic kitchens", reflecting the color of this purer product. The resultant product was approximately 95% (crude) to 99% (refined) arsenic trioxide (Parsons 1925, Hayward 1940, Carapella 1964). Gases that left the white arsenic kitchens were also conveyed to the baghouse. The resultant baghouse dust was returned to the arsenic roaster or refinery furnaces for reprocessing.

The final arsenic trioxide product was conveyed to the arsenic mill, located in the former silver and gold refinery building (Figure 3), where it was ground, sieved, and packaged in barrels for shipment. The mill equipment and arrangement are shown on historic engineering drawings in Attachment A.

### Chronology

Historic engineering drawings (see Attachment A) indicate that the Globe Plant was evaluating various options for arsenic recovery in late 1909. By 1910 or 1911, hand roaster No. 9 in Roaster Building No. 2 (see Figure 3) was dedicated to roasting of baghouse dust for the purpose of concentrating arsenic in the dust. Fumes from this roaster were initially conveyed directly to the blast furnace baghouse. By 1912 or 1913, hand roaster No. 9 was replaced with a more efficient mechanical "arsenic" roaster (see Attachment A), and the fumes were routed through "black arsenic flues", prior to venting to the first 11 rooms of the baghouse through a new, dedicated fan and flue system (Figure 3). The production capacity of the hand roaster was approximately 12 tons per day of ore (EMJ 43, p. 425), while the production capacity of the mechanical roaster was likely in the range of 26 t/d (the capacity of the similar Brown-O'Hara mechanical roasters, see Ingalls 1906, p. 304.)

The arsenic refinery was also constructed around 1910 or 1911, consisting of one furnace and two "white arsenic kitchens" (Figure 3). A second arsenic refining furnace and another kitchen were constructed about 1918.

On June 26, 1919, all operations at the Globe Plant were discontinued, including lead smelting and arsenic refining, until arsenic refining resumed in August 1920 and the third arsenic refinery was constructed. Nevertheless, there was little activity except dismantling of lead smelter and roasting equipment until the spring of 1922, when F. C. Gilbert was placed in charge of by-product recovery and the arsenic roasting and refining furnaces were put back in operation (Sadar 1952). A fourth white arsenic kitchen was added in 1924.

Beginning circa 1920, one or more of the Godfrey roasters in former Roaster Building No.1 was used for roasting lead smelter dust, in addition to the mechanical arsenic roaster. The Godfrey roasters were also connected to the black flues and baghouse.

Arsenic trioxide refining ceased sometime on or around 1926. The arsenic plant buildings, except for the Godfrey Roaster Building, were demolished sometime between 1937 and 1948.

#### Potential for Arsenic Air Emissions

The arsenic recovery and refining process relied upon the capture of sublimated arsenic trioxide particles, primarily within the black arsenic flues and white arsenic kitchens, but also at the baghouse where the roaster gases were ultimately routed. None of the arsenic roaster or furnace emissions were vented by stacks, as this would have caused the release, rather than the collection, of the intended product. As a result, the two principal sources of any air emissions from the arsenic operations were from the baghouse and from fugitive sources.

As discussed above, emissions from the mechanical roaster (initially a hand roaster) and the black arsenic flues were routed to the baghouse, as were the emissions from the

arsenic refining furnaces and white arsenic kitchens. According to Carapella (1964), the fumes leaving white arsenic kitchens are typically 90 percent arsenic trioxide; fumes from the black arsenic flues would likely have had lower arsenic concentrations.

The maximum air flow through the arsenic portion of the baghouse can be estimated from the size of the fan and flue system that conveyed the fumes from all of the arsenic roasters and furnaces to the bags (see drawings in Attachment A). The arsenic portion of the baghouse received gases via a 5 foot diameter steel flue, with 30" diameter headers leading off the flue at right angles into each room of the baghouse. A 10 ft diameter fan operated by a 30 hp motor forced air through the flue. Assuming a maximum reasonable flue air velocity of 2000 fpm, based on good engineering and operating practices (P. Nusz, Asarco) the upper limit for air flow through the arsenic baghouse is calculated to be about 39,000 cfm. Alternatively, the actual air flow rate (acfm) may be calculated from the brake horse power of the fan and the static pressure difference by the following equation:

$$\text{acfm} = (\text{bhp} \times 6356 \times \text{efficiency}) / \text{static head difference}$$

Conservative estimates of fan efficiency and static head are 0.65 and 2 inches, respectively. Therefore, assuming a bhp of 30, the calculated air flow rate is 52,000 acfm. Therefore, a maximum airflow rate in the range of 40,000 to 50,000 acfm is reasonable for the arsenic portion of the baghouse.

Fugitive emissions would have been associated with each of the roaster or furnace buildings, material handling between buildings, and the arsenic mill building, where the refined arsenic trioxide was ground and packaged for shipping. Globe Plant engineering drawings (see Attachment A) show vent hoods over the grinding and packing stations, which appear to recover the product. No vent stack is shown on the drawings.



## **CADMIUM ROASTING AND CALCINING C. 1905 TO 1983**

Lead blast furnace flue dust can also contain certain amounts of cadmium, ranging from 5 to 55 percent, depending on the source of the ore. The early pyrometallurgical procedures for recovery of cadmium from baghouse dust at the Globe Plant are described in an April 1, 1928 document entitled "Outline of Cadmium Process". No author is indicated, but other references from this era suggest it was likely written by Roscoe Teats, the Globe Plant superintendent at the time. According to this document, baghouse dust with sufficient cadmium concentrations was first re-roasted at 825 °C to increase cadmium concentrations to the 40 percent range; because of its lower volatilization temperature, a significant percentage of the arsenic in the dust (20% of the arsenic originally in the dust, according to this document) would also be volatilized along with the cadmium.

Roasting of the cadmium dust was followed by calcining, which involved mixing sulfuric acid with the cadmium dust and heating the mixture in a calcining furnace. The cadmium in the dust would react with the sulfur in the acid to form soluble cadmium sulfate, while lead and other metals would form insoluble sulfates and sulfides. As a result, the soluble cadmium could be leached or washed from the mixture, leaving the other metals behind. Arsenic would tend to be volatilized and emitted from the calcine roaster stack, or would precipitate out with the lead sulfate. After the cadmium sulfate solution was extracted from the calcines, the solution would undergo additional hydrometallurgical purification steps prior to electroplating to recover cadmium metal from the purified solution. Finally, the cadmium metal was melted and re-vaporized in retort furnaces to produce cadmium and cadmium oxide powders. None of the cadmium refining steps after calcining would have had significant arsenic emissions (e.g., see TRC 1988).

### Calcining Operation

According to Iles (1902), cadmium had not been found in the baghouse dust up to the turn of the century; however, low concentrations of cadmium were being recovered from baghouse dust on a small scale as early as 1912 (Sadar 1952). At this time, according to Ambrose (1952), baghouse dust with low cadmium concentrations was processed without

concentration through additional roasting. The initial calcine furnace was a portion of a flue originally used for the former silver and gold refining process, through which cakes of cadmium dust mixed with sulfuric acid were pulled on carts (Ficklin 1952). This flue connected to one of the original 50 foot tall stacks for the former refinery building (e.g., see April 6, 1905 map, Attachment A). The capacity of the process was approximately 2 tons of dust per day (Sadar 1952).

Cadmium recovery operations had increased by 1917 (Ambrose 1952), but the amount of cadmium recovery prior to the cessation of arsenic trioxide refining in 1926 was likely limited, based on the small size of the calcining furnace, the low grade of the cadmium dust, and the accumulation of large stocks of dust by 1926 (Teats 1926).

After the arsenic trioxide refining operation was discontinued in 1926, the Globe Plant was converted to perform larger scale cadmium recovery operations, using lead smelter baghouse dust from other lead smelters for feed stock. The flue calcine furnace in the former silver and gold refinery building was replaced with a larger Herreshoff furnace (No. 1 Calciner) in 1925 (e.g., see Figure 4), followed by two additional Herreshoff furnaces by 1935 (Ambrose 1952). The Herreshoff furnaces initially vented to the 90 foot stack on the north side of the former refinery (now the Calcine) building, then to a 142 foot concrete stack that was constructed circa 1930, according to historic maps (see Figure 5). In 1945 the concrete stack was replaced by the existing 150 foot brick stack.

By 1940, it was recognized that calcining cadmium dust with high arsenic concentrations could result in condensation of arsenic trioxide crystals on the inside of the stack, which could blow out during wind gusts and land on neighboring property within a 500 foot radius (Labbe 1940). In order to evaluate options to control such events, measurements were made during calcining of dust from the Selby smelter which had particularly high arsenic concentration of 9.45 percent (Teats 1940). These measurements indicated that 134,780 pounds of dust were calcined over 248 hours, which contained 12,736 pounds of arsenic based on the arsenic concentration of 9.45 percent. After roasting, the arsenic concentration of the calcines (165,690 pounds of dust plus sulfuric acid) was only 4.2 percent, indicating that 6959 pounds of arsenic were left in the calcines.

Therefore, 5,777 pounds of arsenic, or 45 percent of the arsenic originally in the dust, had volatilized and gone up the stack over the 248 hour period. At a gas flow rate of 10,890 cubic feet per minute (cfm), this represented 0.000036 pounds per cubic foot (pcf) of arsenic, or 0.000047 pcf of arsenic trioxide.

As the gas went up the calcine stack, some of the arsenic trioxide was apparently condensing on the walls near the top of the stack which, therefore, must have been at temperatures lower than the minimum sublimation temperature of arsenic trioxide, or 121° C (250° F). One of the suggestions provided in Labbe (1940) for avoiding a buildup of arsenic trioxide crystals was to occasionally burn additional natural gas to increase the temperature of the stack gases to about 600° F when the wind was blowing from the north. This procedure was intended to sublime the accumulated crystals and cause the resulting arsenic emissions to travel toward the south so that it would not impact neighboring property within 500 feet of the stack which lay to the north. We have not found any references to indicate whether or not Labbe's suggestion was ever implemented.

The arsenic trioxide concentration in gases resulting from the calcining of dusts with lower arsenic concentrations would have been proportionately lower. According to Labbe (1940), dusts from the Murray smelter ranged from 5 to 6 percent arsenic, while Chihuahua and San Luis smelter dusts ranged between 1.5 and 2 percent arsenic. Miles (1970) reported arsenic levels of 2 percent in Chihuahua dust and 0.3 percent in dust from El Paso. Based on mass balance information provided by Miles (1970) and typical arsenic concentrations in gas cleaning solutions that were controlling calcine stack emissions after about 1953 (see TRC 1988), approximately 44 percent of the arsenic in the lower concentration dusts from Chihuahua and El Paso were volatilized in the calcining process. This calculation compares well with the 45 percent value reported by Teats (1940). It should be noted, however, that most of the arsenic in the calcine emissions after 1953 were removed by the mist precipitator and Cottrell gas cleaner.

Calcining operations ceased in 1983, when the pyrometallurgical calcining process was replaced by the hydrometallurgical leaching processes. Arsenic emissions associated with the leaching processes were insignificant (see TRC 1988).

### Godfrey Roaster Operation

By 1926, cadmium was being concentrated in the dust by roasting in Godfrey Roasters, which were connected to the original lead blast furnace baghouse. According to the 1928 "Outline of Cadmium Process" document, 30 one-ton charges (50% dust) were roasted per day at 825 °C. The resultant fumes were captured in the baghouse and contained 35 to 75 percent cadmium, 5 to 15 percent lead, and 2 to 12 percent arsenic. According to Teats (1926), 1,142,800 pounds of dust containing an average 51.8 percent cadmium were processed during the first seven months of 1926, and 10 to 15 percent of the arsenic in the dust was lost in the calcining furnace (the arsenic concentration of the dust was not mentioned).

From about 1926 to the 1950's, the Godfrey Roaster was used to concentrate cadmium in dust from various lead smelters. By the 1960's, however, most of the concentrating was done at the Godfrey Roaster in El Paso, and the Globe Plant roaster was primarily used for recovery of cadmium from calcine and purification muds and residues. The arsenic concentrations in these materials averaged about 1 to 2 percent arsenic (Miles 1970). Further, during the 1950's and later years the Godfrey Roaster was only operated for one to three months a year (e.g., Globe Plant Research Reports, 7/20/51; 12/20/56; 2/7/67; 2/29/70).

Initially, Godfrey Roaster emissions were controlled by the original baghouse for the lead blast furnaces (Figure 4, 1927 through 1930). The original baghouse was replaced in 1947 by a new baghouse (e.g., see Figure 5, 1931 through 1948), which was used to control Godfrey Roaster emissions until the roaster was discontinued in 1977. Gas flow rates to the new baghouse were measured at 63,500 cfm on a hot summer day, when "excessive" amounts of cooling air were added to maintain the gas temperature below 200° F in the baghouse (Donoso 1947); therefore, on more typical cooler days, the gas flow rate would have been lower.

## **HIGH PURITY METALS REFINING**

Only high purity metal, litharge, and bismuth recovery and refining operations have been conducted at the Globe Plant over the past five years. Arsenic emissions associated with these operations, as confirmed by air monitoring data, have been negligible.

Small scale production of arsenic metal by a laboratory plating process was also conducted at the Globe Plant. In this process, arsenic trioxide was purchased as a feed material, rather than being produced as a product. Other than ventilation air, which was controlled by a baghouse, there were no direct air emissions associated with these processes. Arsenic concentrations in the baghouse emissions would have been negligible.

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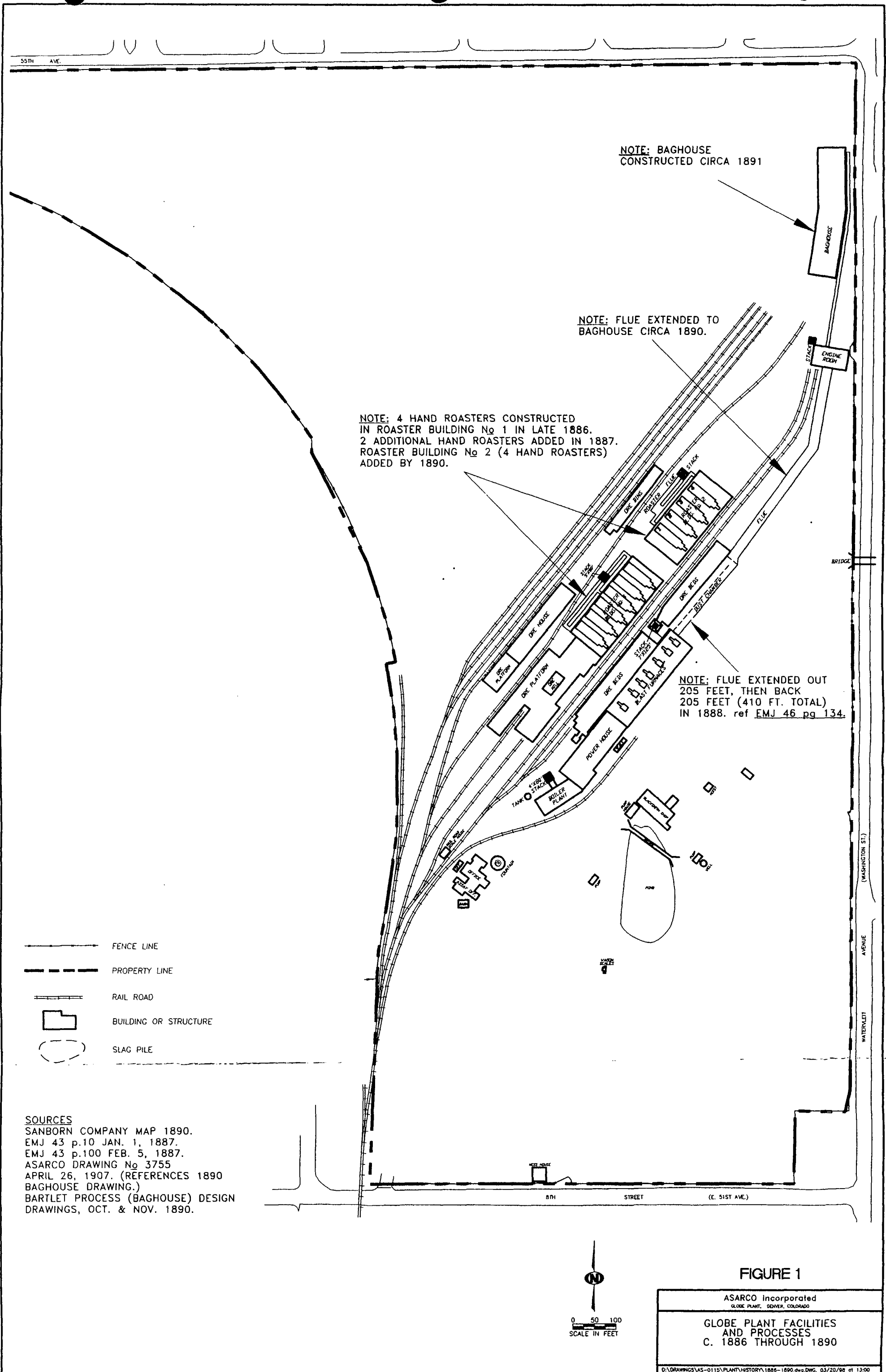
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## FIGURES













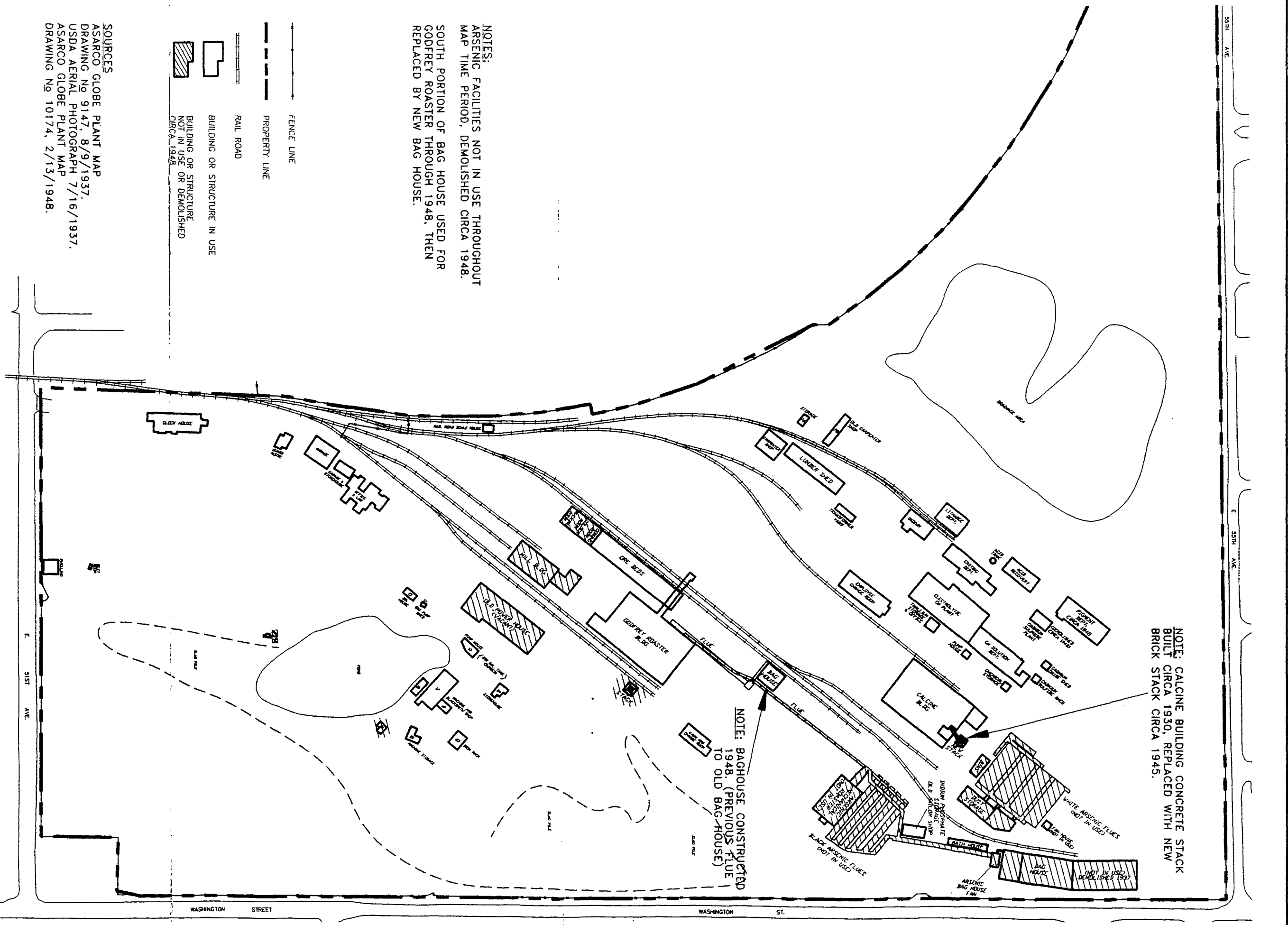


FIGURE 6



**TARGET SHEET**  
EPA REGION VIII  
**SUPERFUND DOCUMENT MANAGEMENT SYSTEM**

DOCUMENT NUMBER: 2007307

SITE NAME: VASQUEZ BLVD./INTERSTATE 70

DOCUMENT DATE: 03/30/1998

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DOCUMENT DESCRIPTION:

ATTACHMENT A - 13 Plant Drawings (See Table of Contents)  
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